

## The nitrogen cycle of tropical montane forest in Ecuador turns inorganic under environmental change

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[1] Water-bound nitrogen (N) cycling in temperate terrestrial ecosystems of the Northern Hemisphere is today mainly inorganic because of anthropogenic release of reactive N to the environment. In little-industrialized and remote areas, in contrast, a larger part of N cycling occurs as dissolved organic N (DON). In a north Andean tropical montane forest in Ecuador, the N cycle changed markedly during 1998–2010 along with increasing N deposition and reduced soil moisture. The DON concentrations and the fractional contribution of DON to total N significantly decreased in rainfall, throughfall, and soil solutions. This inorganic turn of the N cycle was most pronounced in rainfall and became weaker along the flow path of water through the system until it disappeared in stream water. Decreasing organic contributions to N cycling were caused not only by increasing inorganic N input but also by reduced DON production and/or enhanced DON decomposition. Accelerated DON decomposition might be attributable to less waterlogging and higher nutrient availability. Significantly increasing  $\text{NO}_3\text{-N}$  concentrations and  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios in throughfall and litter leachate below the thick organic layers indicated increasing nitrification. In mineral soil solutions, in contrast,  $\text{NH}_4\text{-N}$  concentrations increased and  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios decreased significantly, suggesting increasing net ammonification. Our results demonstrate that the remote tropical montane forests on the rim of the Amazon basin experienced a pronounced change of the N cycle in only one decade. This change likely parallels a similar change which followed industrialization in the temperate zone of the Northern Hemisphere more than a century ago.

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### 1. Introduction

[2] In the past century, the N cycle in the Northern Hemisphere was markedly changed because of domestic, agricultural, and industrial emissions to the environment and purposeful use of mineral fertilizers to increase yields [Van Breemen, 2002; Galloway *et al.*, 2008; Schlesinger, 2009]. In the less industrialized southern hemispheric temperate zone, a much larger part of the water-bound N cycling occurs as dissolved organic nitrogen (DON) [Perakis and Hedin, 2002]. While efforts to reduce N emissions in the industrialized countries stabilized N deposition to ecosystems

at an elevated level, strongly increasing N deposition is expected for the tropics because of economic development and increasing biomass burning [Lara *et al.*, 2001; Galloway *et al.*, 2004, 2008; Boy *et al.*, 2008a]. Therefore, it is likely that even the N cycle of still near-natural, little-disturbed tropical ecosystems at remote locations will change in the near future. These changes might include rising nitrate ( $\text{NO}_3^-$ ) export from terrestrial ecosystems to ground and surface waters, threatening drinking water quality, and increasing eutrophication risks [Matson *et al.*, 1999; Lohse and Matson, 2005; Corre *et al.*, 2010]. Increased availability of the reactive N species ammonium ( $\text{NH}_4^+$ ) and  $\text{NO}_3^-$ , which can be readily taken up by microorganisms and plants in terrestrial systems, should stimulate biomass production in N-limited ecosystems. A possible consequence of increased biomass production is a changed species composition with the risk of loss in biodiversity in the intermediate to long run [Sala *et al.*, 2000; Phoenix *et al.*, 2006]. In the recent literature, evidence has begun to accumulate that these changes are currently occurring in tropical forests as reflected by, e.g., increasing N concentrations and  $\delta^{15}\text{N}$  values in the plant tissue of tropical forests in Panama and Thailand [Hietz *et al.*, 2011].

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[3] The north Andean tropical montane rain forests represent one of the few global diversity hot spots of vascular plants [Barthlott *et al.*, 2007]. The forests of the east exposed eastern cordillera on the rim of the Amazon basin in south Ecuador belong to the most remote continental ecosystems on Earth. They are shielded from the more densely settled inner Andean valleys and coastal areas by the eastern cordillera of the Andes. Because easterly winds prevail, N emissions originating from the west hardly reach these forests. The nearest major urban center and potential source of anthropogenic N to the east is the city of Manaus at a distance of >2000 km. However, the north Andean east exposed forests on the eastern cordillera receive N deposition originating from Amazonian forest fires [Boy *et al.*, 2008a]. Model projections predict a warmer climate for the eastern part of the north Andes, while locally variable positive and negative changes of rainfall (RF) are expected [Vuille *et al.*, 2003; Urrutia and Vuille, 2009]. Increasing temperatures and locally drier conditions could enhance mineralization of soil organic matter, a process frequently limited by waterlogging in tropical montane rain forests, and thus increase bioavailability of N in soil [Schuur and Matson, 2001; Roman *et al.*, 2010].

[4] Many tropical montane forests, including the north Andean forests, are believed to be mainly N limited, although other nutrient limitations may also play a role [Tanner *et al.*, 1998; Wullaert *et al.*, 2010]. However, the view of monoelement limitation of whole ecosystems is currently questioned, particularly for tropical forests [Townsend *et al.*, 2011; Wright *et al.*, 2011]. In a nutrient addition experiment in a tropical montane forest in Ecuador, the joint addition of N and P increased litterfall but decreased fine root biomass. Fine root biomass was also decreased by P addition alone. Microbial biomass and respiration responded most strongly to N addition and tree growth to P addition [Homeier *et al.*, 2012]. The results of Homeier *et al.* [2012] indicate colimitation of litter production and microbial activity by N, although N storages in the organic layer of the studied tropical montane forest in Ecuador (87–2100 g m<sup>-2</sup>) [Wilcke *et al.*, 2002] and N export with stream water (300–500 g m<sup>-2</sup>) [Wilcke *et al.*, 2008] were high. There are reports of a number of manipulative experiments to assess the response of tropical ecosystems to improved biological N availability [Tanner *et al.*, 1998; Corre *et al.*, 2010; Lohse and Matson, 2005; Wullaert *et al.*, 2010; Cusack *et al.*, 2011; Wright *et al.*, 2011]. Hietz *et al.* [2011] concluded from the comparison of archived with recent leaf samples and from the N isotopic composition of dated wood rings that the N cycle of tropical lowland forests changed in the last decades. However, there are only few direct long-term observations of undisturbed old-growth tropical montane forests such as the work of Brookshire *et al.* [2012]. Here we report results of a long-term study of the concentrations and fluxes of NH<sub>4</sub>-N, NO<sub>3</sub>-N, and DON in all major water fluxes of a terrestrial forest ecosystem in south Ecuador during 1998–2010. We hypothesize that (i) total N (TN) deposition increased from 1998 to 2010 as predicted, (ii) the fractional contribution of DON to TN concentrations decreased in ecosystem fluxes, and (iii) trends in NO<sub>3</sub>-N and NH<sub>4</sub>-N concentrations and NO<sub>3</sub>-N/NH<sub>4</sub>-N concentration ratios of ecosystem fluxes indicate changing N turnover processes.

## 2. Materials and Methods

### 2.1. Study Site

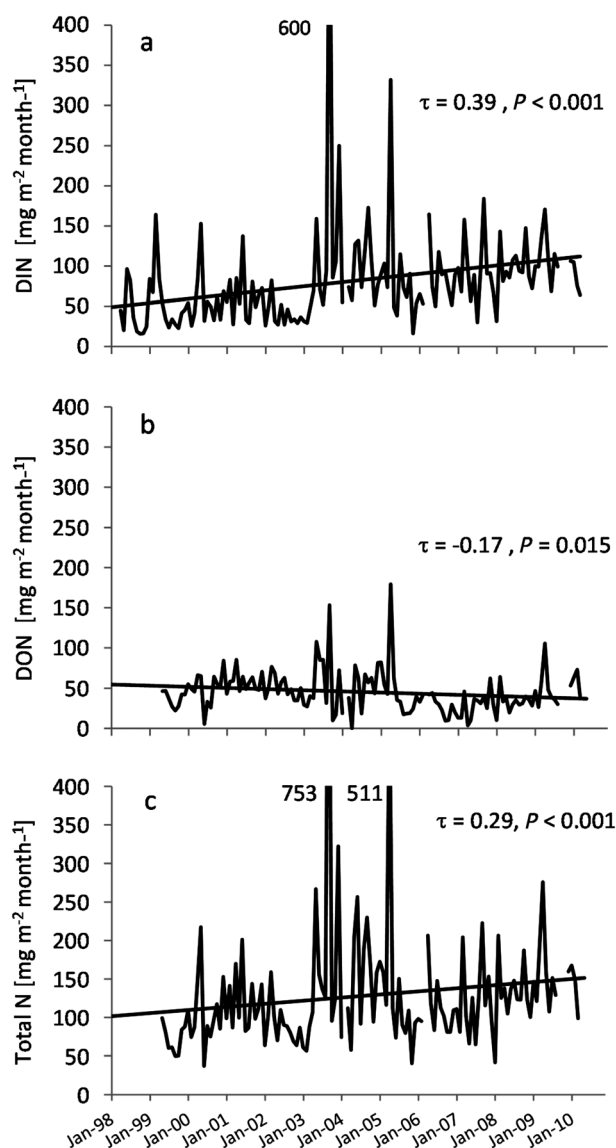
[5] We studied a 30–50° steep, approximately 9.1 ha large microcatchment under an old-growth lower montane rain forest between 1850 and 2200 m above sea level (asl). [Wilcke *et al.*, 2001; Boy *et al.*, 2008b]. Our own records show that annual precipitation ranged between 2000 and 2500 mm and that mean annual temperature was 14.9°C during 1999–2010. Soils are mainly shallow Cambisols developed from metamorphic rock (phyllites and metasandstones). The studied forest can be classified as “bosque siempreverde montaña” (evergreen montane forest) [Balslev and Ollgaard, 2002] or as lower montane forest [Brujinzeel and Hamilton, 2000]. More information on the composition of the forest can be found in the work of Homeier [2004].

### 2.2. Meteorological Conditions and Soil Water Contents

[6] Water volumes of incident precipitation were measured at two to four gauging stations on clear-cut areas each consisting of five permanently open Hellmann-type collectors, thus collecting bulk deposition weekly. We registered additional meteorological conditions at a central station on a clear-cut area in ridgetop position at 1952 masl. Air temperature was measured at a height of 2 m above soil surface with an electronic sensor (Pt100). Relative air humidity was measured with a hygrometer at 2 m above soil surface. All meteorological data were recorded with measuring intervals of 1 h and stored with a data logger (Logger DL 15). To derive synoptic wind directions, we evaluated the National Center for Atmospheric Research reanalysis data [Kalnay *et al.*, 1996]. Furthermore, we calculated 10 day backward wind trajectories at 3000 masl and counted fire pixels in the Amazon along the wind trajectories as described in the work of Rollenbeck *et al.* [2008]. Soil water contents were measured with a frequency domain reflectometry (FDR) probe installed horizontally in the Oa horizon of the organic layer at a measurement station at 1900 masl from May 2000 to November 2007 and at another measurement station at 2070 masl from March 2007 to February 2010. Monthly mean water contents were aggregated from hourly measurements.

### 2.3. Sampling

[7] Between April 1998 and December 2010, we collected throughfall (TF) at three measurement stations under closed canopy (at 1900, 1950, and 2000 masl) with 5–20 fixed-positioned funnel collectors at each measurement station and, additionally, from March 2007 to February 2010 with 400 collectors between 2020 and 2120 masl [Fleischbein *et al.*, 2005; Wullaert *et al.*, 2009]. Furthermore, we sampled at each of the three measurement stations between 1900 and 2000 m asl litter leachate (LL, three zero-tension lysimeters made of plastic boxes with a polyethylene net as a collecting surface area of 0.15 m × 0.15 m, installed below the organic, and soil solutions (SS) at the 0.15 and 0.30 m depths (each depth with three suction cups made of mullite with 1 μm pore size). Stemflow (SF) was sampled with collars at 5 trees. Stream water (SW) was sampled above a weir which was used to gauge streamflow [Boy *et al.*, 2008b]. Throughfall and SF volumes were measured with a graduated cylinder in the field



**Figure 1.** Temporal courses during 1998–2010 of mean monthly (a)  $\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$  = dissolved inorganic N (DIN), (b) dissolved organic N (DON), and (c) total N deposition with rainfall (two to four gauging stations). Temporal trends of monthly data were statistically evaluated with the seasonal Mann-Kendall test [Hirsch *et al.*, 1982]. Regression lines are shown to illustrate significant trends but do not necessarily imply that the trend is linear.

and volume-weighted bulked to result in one bulked sample per measurement station and collection date. Litter leachates and SS were bulked to one individual sample per measurement station and collecting date. All samples were collected in weekly intervals.

## 2.4. Chemical Analyses

[8] Immediately after sampling, the solutions were filtered with ashless filters with a pore size of 4–7  $\mu\text{m}$  (folded filter type 389; Munktell & Filtrak GmbH, Bärenstein, Germany), except the mineral soil solutions which had passed 1  $\mu\text{m}$  pores of the suction cup. After export of the

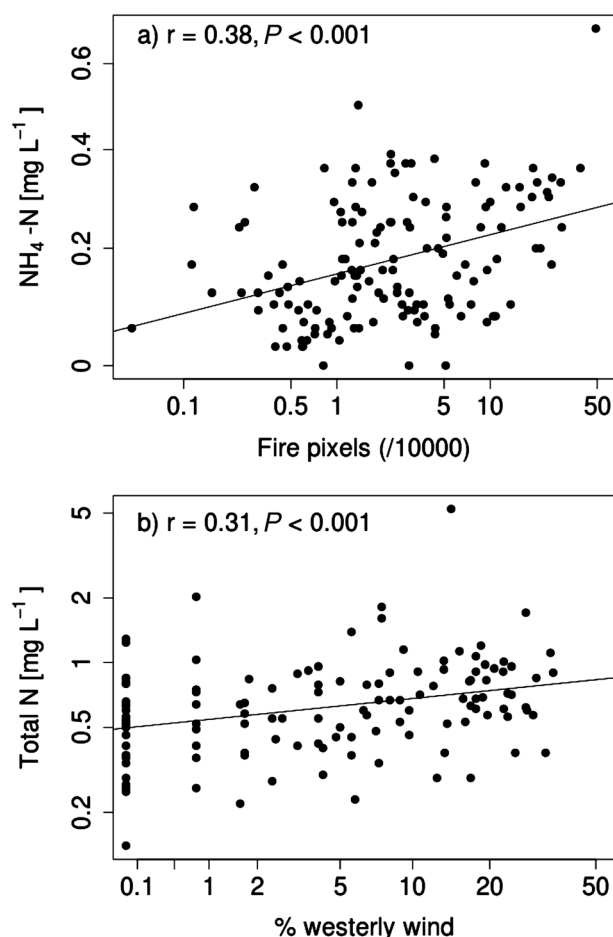
filtered 100 ml aliquots from Ecuador to Germany or Switzerland in frozen state, we determined inorganic N ( $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ , hereinafter  $\text{NO}_3\text{-N}$ ) and total dissolved nitrogen (after UV oxidation to  $\text{NO}_3$ ) colorimetrically with a continuous flow analyzer. The detection limit was 0.075  $\text{mg L}^{-1}$   $\text{NH}_4\text{-N}$  or  $\text{NO}_3 + \text{NO}_2\text{-N}$ . Boy *et al.* [2008a] tested the stability of the sample during the 1 week that the collected solutions remained in the field and did not detect N transformations in the solutions. Concentrations and composition of N species ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and DON) in samples which remained a week in the field compared well with mean weekly concentrations calculated from daily sampling at the same site parallel to the weekly sampling [Boy *et al.*, 2008a].

## 2.5. Calculations and Statistical Analyses

[9] Dissolved organic nitrogen concentrations were calculated as the difference between TN and the sum of total inorganic nitrogen [ $\text{NH}_4^+ + \text{NO}_3^-$ , dissolved inorganic N (DIN)] concentrations. Monthly mean concentrations were calculated by arithmetically averaging weekly concentrations. Monthly fluxes were calculated by multiplying monthly mean concentrations with monthly water fluxes. Rainfall, TF, and SF rates were directly measured. Water fluxes in soil were calculated with a water budget model based on water content measurements with FDR probes. Streamflow was calculated with a catchment model [Boy *et al.*, 2008b]. Monthly values were summed up from weekly measurements, except for streamflow which was modeled in hourly resolution. Correlation analyses followed the least squares method after data transformation to reach normal distribution if necessary. Trends in monthly data series were determined with the seasonal Mann-Kendall test [Hirsch *et al.*, 1982] using the package *Kendall* [McLeod, 2011] in R [R Development Core Team, 2011]. The seasonal Mann-Kendall test is a nonparametric trend test considering the most important autocorrelation (i.e., seasonal) which we detected. The test is not sensitive to a small number of outliers. The application of the test does not necessarily require a linear trend [Helsel and Hirsch, 2002]. The linear regression lines in our graphs are meant to facilitate a fast recognition of significant trends. Breakpoints in our time series were analyzed with the sequential Mann-Kendall test using the function *seqMK()* of the package *pheno* in R [R Development Core Team, 2011].

## 3. Results

[10] Dissolved inorganic N and TN deposition in rainfall increased significantly during 1998–2010, while DON deposition decreased significantly (Figure 1). Figures 1a and 1c suggest that there is a potential breakpoint in the year 2003, but our breakpoint analysis did not reveal a significant breakpoint in 2003 for DIN and TN. The number of fire pixels showed a significant positive trend during 1998–2010 (seasonal Mann-Kendall test,  $\tau = 0.53$ ,  $P < 0.001$ ). The number of fire pixels correlated significantly positively with  $\text{NH}_4^+\text{-N}$  (Figure 2a),  $\text{NO}_3\text{-N}$  ( $r = 0.32$ ,  $P < 0.001$ ), and DIN ( $r = 0.37$ ,  $P < 0.001$ ) concentrations in RF and, hence, negatively with the fractional DON contribution to TN concentrations ( $r = -0.26$ ,  $P = 0.003$ ). Between 1998 and 2010, the frequency of the synoptic westerly winds at the atmospheric altitude of 500 hPa increased significantly (seasonal Mann-Kendall test,  $\tau = 0.19$ ,  $P = 0.003$ ).



**Figure 2.** Relationships between (a) the number of fire pixels along 10 day backward wind trajectories at 3000 m asl over the Amazon basin and the  $\text{NH}_4\text{-N}$  concentrations in rainfall (two to four gauging stations) and (b) the frequency of westerly wind at 50 MPa and the total N concentrations in rainfall (two to four gauging stations). Fire pixels and total N concentrations in rainfall were log and percentages of westerly wind  $\log(x+1)$ -transformed to approximate normal distribution as prerequisite for parametric correlation and regression analysis. From the  $\text{NH}_4\text{-N}$  data set, we removed one outlier (out of 139 values) of  $2.2 \text{ mg L}^{-1}$ .

The frequency of westerly winds correlated significantly positively with TN concentrations in RF (Figure 2b).

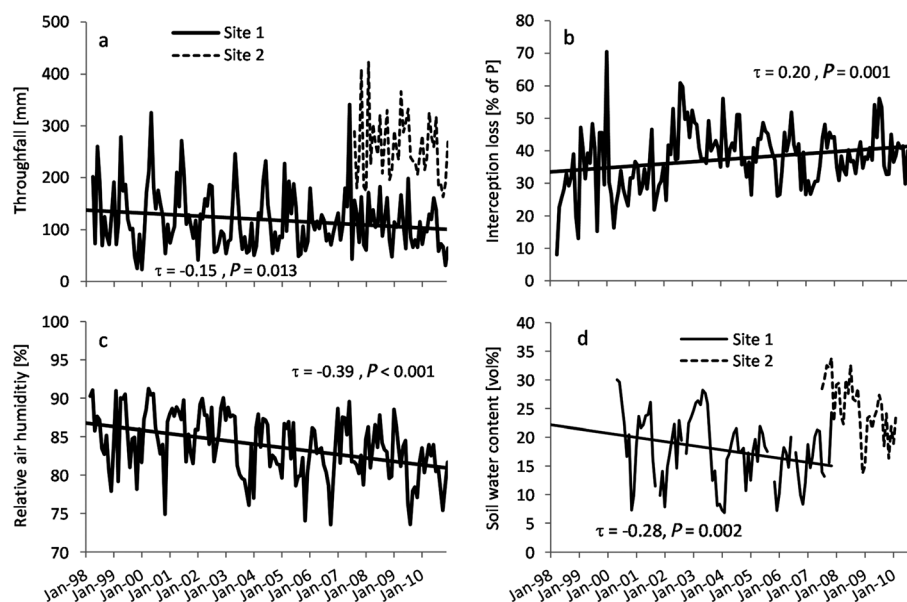
[11] Besides the changing rates and composition of the N deposition to our study site, we observed a number of simultaneously occurring hydrological changes. While monthly rainfall did not change during 1998–2010 at our study site (not shown), there was a significant decrease in TF at 1900–2000 m asl (Site 1, Figure 3a). At 2060–2130 m asl (Site 2), we also observed decreasing TF, but the trend at Site 2 was not significant. No trend in RF and a significant negative trend in TF resulted in a significant increase of the interception loss (in % of RF). Furthermore, relative air humidity in the forest significantly decreased during 1998–2010 (Figures 3b and 3c). The resulting increasingly dry microclimatic conditions were reflected by the decreasing water contents in the Oa horizon of the organic layer at 1900 m asl during 2000–2007 (Figure 3d). Another record of water contents in the Oa horizon of the

organic layer at 2070 m asl during 2007–2010 also showed a decrease, although this trend was not significant. Moreover, monthly hours of extreme temperatures  $>25^\circ\text{C}$  increased significantly during 1998–2010 (seasonal Mann-Kendall test,  $\tau=0.30$ ,  $P<0.001$ ), pointing at an increasing evaporative demand which likely contributed to the increasing soil dryness.

[12] Dissolved organic N occurred in all solutions of the forest ecosystem (Figure 4a). It was deposited with RF, and concentrations increased along the path of the water through the ecosystem until the surface of the mineral soil was reached. The canopy was a major source of DON in the studied ecosystem. In the mineral soil, DON concentrations decreased, and the lowest DON concentrations occurred in SW. When comparing Figures 4a and 4b, it becomes evident that the vertical distribution of DON concentrations and fractional DON contributions to TN concentrations was similar in all ecosystem solutions, except SF. Stemflow had the largest fractional contribution of DON to TN, but the second highest DON concentration. The  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios increased along the flow path of water from RF through the forest (except for SF) to the mineral soil where they were highest and decreased towards SW (Figure 4c). In the mineral soil, both  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  concentrations and fluxes were consistently the lowest of all ecosystem solutions (Table 1) in line with previous reports by Goller *et al.* [2006] and Schwarz *et al.* [2011]. Total N fluxes increased along the water path through the aboveground part of the ecosystem. However, in SW, total N fluxes were markedly lower than in RF (Figure 4d). Mean annual deposition rates of N with rainfall during the observation period amounted to  $1.2 \text{ g m}^{-2} \text{ yr}^{-1}$ . In TF (which includes an unknown contribution of dry particulate and gaseous deposition), the mean annual flux increased to  $2.5 \text{ g m}^{-2} \text{ yr}^{-1}$ , while only  $0.38 \text{ g m}^{-2} \text{ yr}^{-1}$  was, on average, exported with SW.

[13] The only significant temporal trend in TN concentrations of the ecosystem solution was detected in RF (Figure 5a). There were significant negative temporal trends of the fractional DON contribution to TN in all ecosystem solutions, except SF and SW. The strength of the trend of the fractional DON contribution to TN based on Kendall's  $\tau$  was most pronounced in RF and TF and gradually decreased along the flow path of water through the system (SF disregarded) until the trend disappeared in SW. The negative trend in the fractional contribution of DON to TN was a consequence of both increasing DIN concentrations (Table 1; at least one of  $\text{NH}_4^+$  or  $\text{NO}_3^-$  concentrations increased significantly in all ecosystem solutions, except SF) and decreasing DON concentrations during 1999–2008 in all ecosystem solutions, except SF and SW. Measured by Kendall's  $\tau$ , the negative DON concentration trends in RF, TF, and LL had similar strengths ( $\tau=-0.19$  to  $-0.23$ ,  $P=0.004$ – $0.008$ ,  $n=94$ – $126$ ), while the trends were more pronounced in mineral SS (SS15, SS30,  $\tau=-0.31$  to  $-0.48$ ,  $P<0.001$ ). Because our time series had different durations, we also tested the period April 2000 to March 2008 for which data were consistently available for all ecosystem solutions. There were only small changes in  $\tau$  and  $P$  values, except that the TN concentrations in RF did not show a significant trend during April 2000 to March 2008.

[14] To assess shifting N transformation processes during the observation period, we also evaluated time series of  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios. The  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios showed significant negative trends in



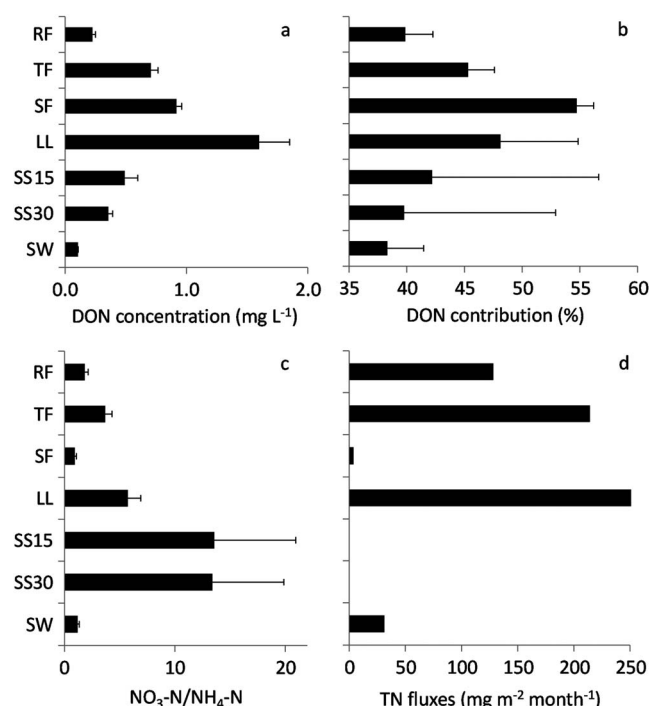
**Figure 3.** Temporal courses of mean monthly (a) throughfall at two sites (three gauging stations with 5–20 collectors during 1998–2010 at 1900–2000 masl and one gauging station with 400 collectors during 2007–2010 at 2020–2120 masl), (b) interception loss (in % of rainfall) during 1998–2010, (c) relative air humidity during 1998–2010, and (d) soil water contents in the organic layer at two sites (frequency domain reflectometry probe at 1900 m above sea level (asl) from 2000 to 2007 and at 2070 m asl in the same study area during 2009–2010). Temporal trends of monthly data were statistically evaluated with the seasonal Mann-Kendall test [Hirsch *et al.*, 1982]. Regression lines are shown to illustrate significant trends but do not necessarily imply that the trend is linear.

RF and SS at the 0.15 m and 0.30 m depths and significant positive trends in TF and LL (Figure 6). We also tested the time series of  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios for the shorter observation period (April 2000 to March 2008) for which we had complete data sets. The trends for  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios in RF, LL, and SW were similar. During April 2000 to March 2008, however, there was no significant trend in  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios in TF but, instead, a significant negative trend in  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios in SF (seasonal Mann-Kendall test,  $\tau = -0.20$ ,  $P = 0.020$ ).

#### 4. Discussion

[15] The significant increase in DIN deposition with rainfall during 1998–2010 by almost 100% from  $0.5\text{--}0.6\text{ g m}^{-2}\text{ yr}^{-1}$  in the first 3 years of measurement to approximately  $0.9\text{--}1.0\text{ g m}^{-2}\text{ yr}^{-1}$  in the last 3 years supports our first hypothesis. This finding is in line with predictions by Galloway *et al.* [2004] that there will be rising N deposition in the study region, particularly because of rising DIN deposition (Figure 1a). At our study site,  $\text{NH}_4^+$  contributed more to the increase in DIN deposition than  $\text{NO}_3^-$  as reflected by the significant decrease in  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratio in RF (Figure 6), while concentrations of both  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  significantly increased (Table 1). However, the predicted deposition for the study area in the year 2050 of  $1.0\text{--}2.0\text{ g m}^{-2}\text{ yr}^{-1}$  [Galloway *et al.*, 2004] seems to be almost reached by 2010. A similar increase in DIN deposition was observed in Europe during the 1900s which plateaued in the 1970s and 1980s and thereafter remained constant or even decreased slightly [Matzner and Meiwes, 1994; Wright *et al.*, 2001; Matzner *et al.*, 2004].

Forested mountainous areas in central and southeast Germany currently receive between  $1$  and  $2\text{ g m}^{-2}\text{ yr}^{-1}$  of DIN as bulk deposition [Matzner and Meiwes, 1994; Matzner *et al.*, 2004]. In the Hubbard Brook Experimental Forest in the northeastern U.S., with its globally longest reported continuous deposition record, an increase from approximately  $0.3$  to  $0.7\text{ g m}^{-2}\text{ yr}^{-1}$  of DIN deposition with rainfall was observed in the 1960s with no major changes thereafter until 2008 [Bernal *et al.*, 2012]. Thus, the current DIN deposition at our study site in Ecuador ranges between that at Hubbard Brook and the rather remote German middle mountain areas. If it were assumed that the annual N accretion in aboveground biomass is similar to the  $0.5\text{--}0.9\text{ g m}^{-2}\text{ yr}^{-1}$  reported for forests in Puerto Rico [McDowell and Asbury, 1994], the current DIN deposition would be sufficient to cover the whole N accretion in aboveground biomass. However, DIN (and TN) deposition is still small compared with the high N storage in the whole ecosystem which makes it difficult to detect a signal that is small compared to N pools and circulation in the ecosystem. The organic layer alone stored, on average,  $553\text{ g m}^{-2}$  of N [Wilcke *et al.*, 2002]. Although DON deposition decreased by approximately 20% from approximately  $0.5\text{ g m}^{-2}\text{ yr}^{-1}$  in the first 3 years (starting in 1999 when DON was measured for the first time) to approximately  $0.4\text{ g m}^{-2}\text{ yr}^{-1}$  in the last 3 years of measurement (Figure 1b), TN deposition still increased significantly by approximately 40% between 1999 and 2010 from approximately  $1.0$  to  $1.4\text{ g m}^{-2}\text{ yr}^{-1}$  (Figure 1c). Deposition rates of DON are rarely reported. Michalzik *et al.* [2001] summarized bulk DON deposition rates of approximately  $0.1\text{--}0.5\text{ g m}^{-2}\text{ yr}^{-1}$ , while at Hubbard Brook, about  $0.1\text{--}0.2\text{ g m}^{-2}\text{ yr}^{-1}$  were observed



**Figure 4.** (a) Mean concentrations of dissolved organic nitrogen (DON), (b) mean fractional DON contributions to total N concentrations, (c) mean  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios, and (d) mean total N (TN) fluxes in the major ecosystem solutions (RF, rainfall; TF, throughfall; SF, stemflow; LL, litter leachate; SS15, mineral soil solution at 0.15 m depth; SS30, mineral soil solution at 0.30 m depth; SW, stream water) of a tropical montane rain forest in Ecuador during 1998–2008 (RF: until 2010). Error bars depict standard errors of the means of two to four gauging stations (RF) or three measurement stations of all other fluxes, except SF (five trees). Fluxes were calculated in an area-representative way for a whole approximately 9 ha large microcatchment without replication. No flux data were available for the mineral soil (SS15, SS30).

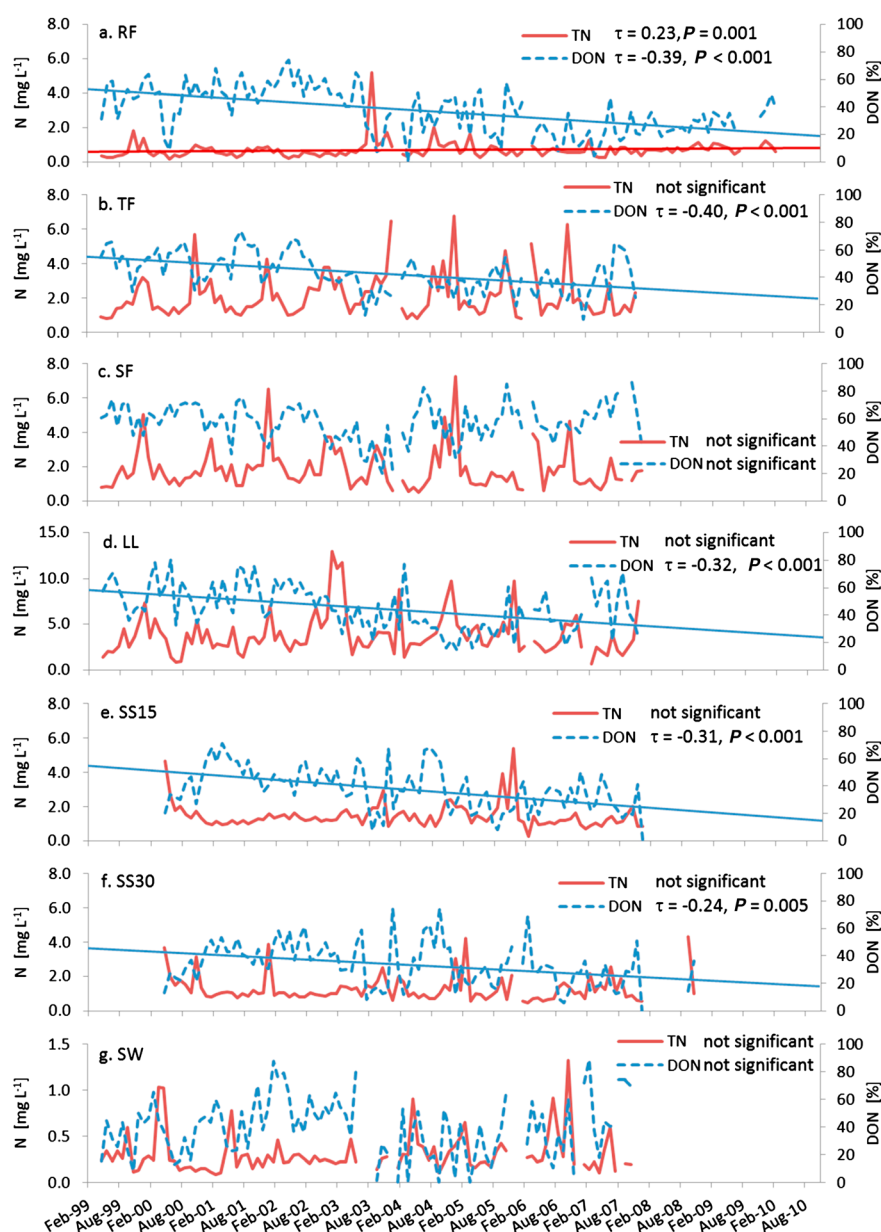
between 1995 and 2008 [Bernal *et al.*, 2012]. Thus, our DON deposition rates were at the upper end of the range reported in the literature which might be related to the fact that the Amazon forest canopy releases considerable amounts of volatile organic matter likely including compounds showing up as DON in our rainfall samples [Forti and Neal, 1992].

[16] To assess the reasons for strongly increasing DIN and slightly decreasing DON deposition rates, we investigated the relationship between N deposition and environmental changes observed in the study area, including increasing fire activity in the Amazon basin, changing synoptic wind directions, and changing local land use. Our finding of significant positive correlations of the concentrations of individual DIN species with number of fire pixels (Figure 2a) was already reported for the study area (albeit only for a 5 year period) by Boy *et al.* [2008a]. This correlation supports the assumption that an increasing fire activity in the Amazon basin, as illustrated by the significantly increasing trend in number of fire pixels, contributed to increase DIN deposition. At the same time, the fire activity changed the chemical quality of N deposition to increasing DIN contributions at the expense

of DON. The increasing frequency of westerly winds also increased TN deposition, particularly in October and November when westerly winds prevailed during up to 40% of the time. In addition to Amazon forest fires and changing synoptic wind directions, the accelerated local land use change in the wider study area could be a source of increasing N deposition to our study area. In a 4800 km<sup>2</sup> large area around the cities of Zamora and Loja, the forest area decreased by approximately 342 km<sup>2</sup> (i.e., 13.6% of approximately 2500 km<sup>2</sup> in 1987), while the area covered by grassland, settlement, and other land uses increased by approximately 228, 2.2, and 112 km<sup>2</sup>, respectively [Peters *et al.*, 2013]. Known consequences of such land use changes are increasing vehicular traffic, fertilizer use, and agricultural and domestic emissions which all constitute potential sources of N deposition to our study area. The practice of converting native forest to pasture by slash-and-burn clearing suggests that extremes in DIN deposition are related to local fires.

[17] Simultaneously to the changes in quantity and quality of N deposition, we observed reduced humidity in this humid forest (Figure 3), although total annual rainfall did not change significantly. The usual high soil water contents contribute to the accumulation of thick organic layers in the study area because temporal waterlogging reduces organic matter mineralization [Schuur and Matson, 2001; Wilcke *et al.*, 2002; Roman *et al.*, 2010]. Our finding of decreasing soil water contents at two measurement stations in the study region (Figure 3d) is corroborated by the finding of Wilcke *et al.* [2013] that the frequency of waterlogged conditions decreased during 1998–2010. Wilcke *et al.* [2013] recorded soil matric potentials at the 0.15 and 0.30 m mineral soil depths at Site 1 in Figure 3a with manually read tensiometers. Reduced humidity could be driven by the temperature increases predicted by Vuille *et al.* [2003] and Urrutia and Vuille [2009], which have been confirmed for the greater study area with the help of a time series since 1964 [Peters *et al.*, 2013]. Increasing temperatures created an increasing evaporative demand, while rainfall did not change. Furthermore, Peters *et al.* [2013] observed an increasing number of dry periods lasting for 4–14 days between 1998 and 2010, during which evaporation was pronounced and could have driven both increasing interception losses and decreasing soil water contents. The increasing number of dry periods is also reflected by our finding that there was a more frequent occurrence of extreme temperatures above 25°C. Reduced waterlogging could potentially increase the time period during which favorable conditions for turnover of soil organic matter prevailed. The resulting enhanced N mineralization would add to the N enrichment by deposition from the atmosphere. Consequently, there were two marked changes of environmental conditions in our study area, consisting of increasing DIN availability and reduced waterlogging which likely influenced the whole N cycle of the studied tropical montane forest ecosystem.

[18] If there was just an addition of DIN to the ecosystem fluxes by increasing DIN deposition and by enhanced ammonification in soil, the fractional contribution of DON would decrease, while DON fluxes would remain unchanged. Furthermore, the effect of DIN addition should be strongest in TF, SF, and LL and weaker in SS and SW because of the late position of SS and SW in the pathway of rainwater through the ecosystem. Figure 5 illustrates that this is what



**Figure 5.** Mean temporal course of total N (TN) concentrations and fractional dissolved organic N (DON) contributions to TN during 1999–2008 (RF: until 2010) in (a) rainfall (RF,  $n = 2$ –4), (b) throughfall (TF,  $n = 3$ ), (c) stemflow (SF,  $n = 5$ ), (d) litter leachate (LL,  $n = 3$ ), (e) mineral soil solution at 0.15 m depth (SS15,  $n = 3$ ), (f) mineral soil solution at 0.30 m depth (SS30,  $n = 3$ ), and (g) stream water (SW,  $n = 1$ ). Temporal trends of monthly data were statistically evaluated with the seasonal Mann-Kendall test [Hirsch *et al.*, 1982]. Regression lines are shown to illustrate significant trends but do not necessarily imply that the trend is linear. Mind the different left Y axis scaling.

we observed, suggesting that the addition of DIN is indeed one possible reason for decreasing fractional DON contributions to TN during 1998–2010. However, further to the DIN addition effect, there was also a significant decrease in DON concentrations which was less pronounced in the aboveground part of the ecosystem (canopy and soil organic layer) than in the mineral soil. This suggests that there was also a change in N transformations. The reason why this change in N transformation appears to be less strong in the aboveground part of the ecosystem than in the mineral soil might be related with the fact that the major sources of DON are located in the

aboveground part, and thus, a small change in DON concentrations is more difficult to detect (Figure 4). We assume that epiphyllic microorganisms, epiphytes, leaching of plant tissue, and soil-like accumulations in the canopy acted as a source of DON in TF and SF. The organic layer had the highest organic matter and nutrient concentrations and hosted most plant roots of the whole ecosystem, resulting in pronounced biological activity [Wilcke *et al.*, 2002; Soethe *et al.*, 2006], and therefore was the largest source of DON (Figure 4) [Goller *et al.*, 2006].

[19] Decreasing DON concentrations can be explained by reduced DON production, e.g., by less leaching of organic



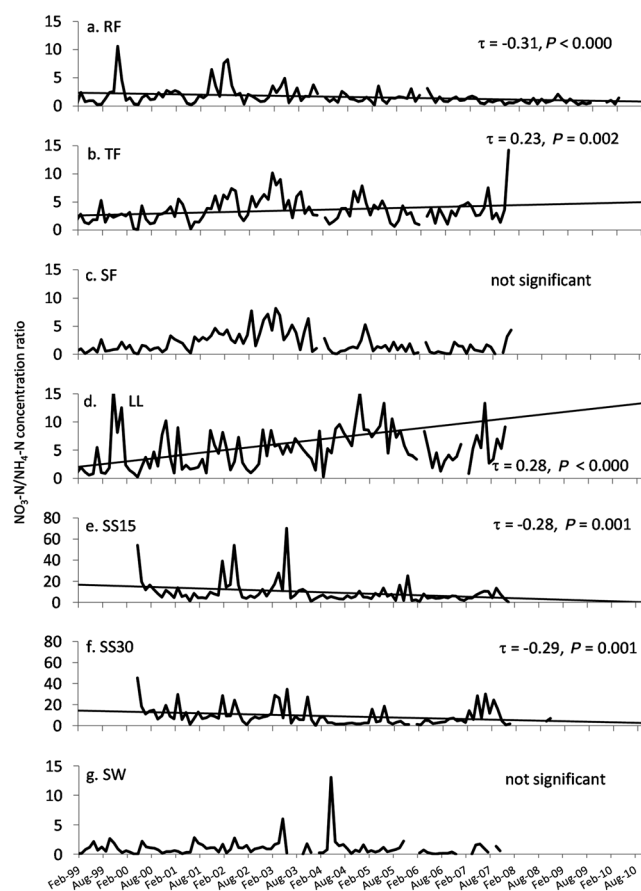
**Table 1.** Concentrations of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  Averaged Across Replicate Measurement Stations in Rainfall (RF, Two to Four Measurement Stations/Data From 139 Months), Throughfall (TF, 3/115), Stemflow (SF, 5/115), Litter Leachate (LL, 3/115), Mineral Soil Solution at 0.15 m Depth (SS15, 3/94), Mineral Soil Solution at 0.30 m Depth (SS30, 3/94), and Stream Water (SW, 1/108) and Significant ( $P < 0.05$ ) Kendall's  $\tau$  Values Calculated With the Seasonal Mann-Kendall Test [Hirsch *et al.*, 1982] for the Time Series From 1998 to 2008 (RF: Until 2010, Monthly Values Calculated as Arithmetic Means of Weekly Measurements)

	$\text{NH}_4\text{-N}$			$\text{NO}_3\text{-N}$		
	( $\text{mg L}^{-1}$ )	Kendall's $\tau$	$P$	( $\text{mg L}^{-1}$ )	Kendall's $\tau$	$P$
RF	0.20	0.486	<0.000	0.25	0.168	0.011
TF	0.36			1.00	0.227	0.002
SF	0.36			0.57		
LL	0.45			1.86	0.159	0.031
SS15	0.13	0.290	0.001	0.84		
SS30	0.13	0.217	0.011	0.79		
SW	0.12	0.174	0.027	0.08		

matter in the canopy or the organic layer or by less production of microbial N compounds or root exudates. Alternatively, DON decomposition might have been enhanced because of stimulated microbial activity. Furthermore, the significant decrease in pH of LL during 1999–2008 ( $\tau = -0.17$ ,  $P = 0.031$ ,  $n = 127$ ) caused more positively charged surface sites of soil solid phase and protonated dissolved organic matter (DOM). Positively charged surface sites might have adsorbed more of the negatively charged DOM, including N-containing compounds and increased protonation of negatively charged functional groups of DOM. Thereby, DON solubility was likely also reduced [Michalzik *et al.*, 2001]. Soil acidification resulted from direct acid deposition originating from Amazonian forest fires [Boy *et al.*, 2008a]. An additional acidification might have resulted from nitrification and subsequent  $\text{NO}_3^-$  leaching from the organic layer which increased in the observation period [Wilcke *et al.*, 2013]. The fact that DON concentrations in SW were strongly influenced by fast lateral flow through the organic layer during storm events [Goller *et al.*, 2005, 2006; Boy *et al.*, 2008b] likely explains why neither DON concentrations nor fractional contributions of DON to TN in SW showed temporal trends (Figure 5). We did not observe a change in SW water fluxes nor in the water level distribution during the observation period (not shown), which explains why the DON concentrations in SW remained stable. A higher contribution of DON leached to the stream by near-surface flow in soil might explain why the fractional contributions of DON to TN in the studied SW were higher than in several streams draining tropical montane forests in Costa Rica and the Caribbean, where DON contributed, on average, 15% to TN concentrations [Brookshire *et al.*, 2012]. The elevated DIN input which was higher than in the Hubbard Brook Forest in the northeastern U.S. is a possible reason for lower fractional DON contributions to TN concentrations in SW at our study site than in a large number of remote temperate streams in South America (with presumably lower DIN inputs) where mean fractional DON contributions of 80% were reported [Perakis and Hedin, 2002]. Remarkably, the contribution of  $\text{NH}_4\text{-N}$  to TN in SW was with an average of 38% at the upper end of observations in temperate streams of South America [Perakis and Hedin, 2002]. It was

also much higher than in streams draining tropical montane forests in Central America and the Caribbean where only contributions <5% were found [Brookshire *et al.*, 2012]. We attribute this finding to overall less pronounced nitrification in our study soils because of higher water contents and the fact that the more pronounced near-surface flow besides DON also carries high  $\text{NH}_4^+$  loads to the stream [Boy *et al.*, 2008b]. In contrast to many of the studied forests in Brookshire *et al.* [2012], there is no pronounced dry season favoring nitrification in our study area. Low nitrification rates are corroborated by the results of a  $^{15}\text{N}$  tracer experiment in our study area which revealed that nitrification was only measurable after experimental addition of  $10 \text{ g m}^{-2}$  of N (as urea) or after simultaneous addition of  $5 \text{ g N}$  and  $1 \text{ g P m}^{-2}$  (as  $\text{NaH}_2\text{PO}_4$ ) [Martinson *et al.*, 2013].

[20] The decrease in DON concentrations in many ecosystem solutions underlines that the environmental changes of the past decade did not only result in the addition of more DIN but also influenced N transformations in the studied ecosystem. A further clue toward understanding these changes



**Figure 6.** Mean temporal course of  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios during 1999–2008 (RF: until 2010) in (a) rainfall (RF,  $n = 2\text{--}4$ ), (b) throughfall (TF,  $n = 3$ ), (c) stemflow (SF,  $n = 5$ ), (d) litter leachate (LL,  $n = 3$ ), (e) mineral soil solution at 0.15 m depth (SS15,  $n = 3$ ), (f) mineral soil solution at 0.30 m depth (SS30,  $n = 3$ ), and (g) stream water (SW,  $n = 1$ ). Temporal trends of monthly data were statistically evaluated with the seasonal Mann-Kendall test [Hirsch *et al.*, 1982]. Regression lines are shown to illustrate significant trends but do not necessarily imply that the trend is linear. Mind the different Y axis scaling.



can be obtained from an analysis of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  concentrations in the ecosystem solutions. However, it must be borne in mind that the N cycle is complex and that there may be various simultaneously occurring processes explaining changes in the  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  concentrations in ecosystem solutions. The work of Schwarz *et al.* [2011], who used a  $^{15}\text{N}$  stable isotope approach in  $\text{NO}_3^-$ , has shown that in the forest canopy and the organic layer, strong nitrification occurs which explains increasing  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios from RF to TF and from LL to SS15 (Figure 4). It seems, therefore, reasonable to assume that the significantly increasing  $\text{NO}_3\text{-N}$  concentrations and increasing  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios in TF and LL during 1998–2010 (Table 1 and Figure 6) are caused by enhanced nitrification. This is particularly likely because nitrification seems to be less pronounced in our study ecosystem than in comparable ecosystems in Costa Rica (Brookshire *et al.*, 2010), leaving more opportunity for enhancement. In the canopy, we suggest that the increasing availability of  $\text{NH}_4^+$  enhanced nitrification because  $\text{NH}_4^+$  availability is the most important driver of nitrification [Robertson, 1989; Avrahami *et al.*, 2002; Booth *et al.*, 2005]. The reduced duration of waterlogging while the organic layer was nevertheless rarely completely dry (Figure 3d) likely increased nitrification rates because  $\text{O}_2$  availability is an additional driver of nitrification [Robertson, 1989]. The assumption of enhanced nitrification in the canopy and the organic layer is also supported by the fact that TF and LL were the only ecosystem solutions in which  $\text{NO}_3\text{-N}$  concentrations increased significantly during 1998–2008. At the same time,  $\text{NH}_4\text{-N}$  concentrations did not show a temporal trend in spite of the rising  $\text{NH}_4\text{-N}$  deposition (Table 1). In the mineral soil solutions, in contrast,  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios decreased (Figure 6), while at the same time,  $\text{NH}_4\text{-N}$  concentrations increased and  $\text{NO}_3\text{-N}$  concentrations did not show a temporal trend (Table 1). We therefore suggest that  $\text{NH}_4^+$  was produced in the mineral soil by enhanced net ammonification favored by the reduced duration of waterlogging [Schnoor and Matson, 2001; Roman *et al.*, 2010], which was, however, not followed by detectable enhanced nitrification. We speculate that the fact that this increased release of  $\text{NH}_4^+$  obviously did not increase  $\text{NO}_3\text{-N}$  concentrations in SS - different to the canopy and the organic layer - is related with the large difference in N availability in the organic layer and the mineral soil. This large difference in N availability likely resulted in different microorganism community compositions which is also reflected by the much higher  $\text{NO}_3\text{-N}/\text{NH}_4\text{-N}$  concentration ratios in SS than in LL. The mean N concentration of 47 soils in the study area dropped from  $23 \text{ g kg}^{-1}$  in the organic layer to  $3.4 \text{ g kg}^{-1}$  in the mineral soil [Boy *et al.*, 2008b]. Furthermore, the mineral soil is consistently moister than the organic layer (own unpublished results), causing a more pronounced  $\text{O}_2$  scarcity for nitrification. Increased net ammonification might also explain the significant positive trend in  $\text{NH}_4\text{-N}$  concentrations of the SW because of leaching (Table 1).

[21] Finally, net accumulation of deposited N would further point to changing N processes because accumulation includes biological immobilization of N besides abiotic retention mainly of  $\text{NH}_4^+$  on cation exchanger sites or by fixation in illites which are abundant in the studied soils [Schrumpp *et al.*, 2001]. The mean difference between N fluxes with RF and SW of approximately  $0.8 \text{ g m}^{-2} \text{ yr}^{-1}$

during the observation period was considerably larger than the roughly estimated  $60 \text{ mg m}^{-2} \text{ yr}^{-1}$  of  $\text{N}_2\text{O-N} + \text{NO-N}$  emissions reported by Wolf *et al.* [2011] for our study site. Using the ratio of  $\text{N}_2\text{O-N}/(\text{N}_2\text{O-N} + \text{N}_2\text{-N})$  for tropical forest of Bai *et al.* [2012] gives an estimate of  $213 \text{ mg m}^{-2} \text{ yr}^{-1}$  for the  $\text{N}_2\text{-N}$  losses by denitrification. The ratio of  $\text{N}_2\text{O-N}/(\text{N}_2\text{O-N} + \text{N}_2\text{-N})$  of Bai *et al.* [2012] was modeled for a large scale based on the natural abundance of stable N isotopes. Even if an additional small contribution of NO-N to denitrification losses is considered adding up to a total gaseous N loss of  $<0.3 \text{ g m}^{-2}$ , our results indicate that most deposited N is accumulated in the ecosystem in line with previous findings [Boy *et al.*, 2008a; Wullaert *et al.*, 2010]. Given the changes in soil water contents (Figure 3d), there might be increasing  $\text{NO-N} + \text{N}_2\text{O-N}$  losses because of enhanced nitrification, while the  $\text{NO-N} + \text{N}_2\text{O-N}$  losses via denitrification rather tend to decrease because of higher soil redox potentials as a consequence of reduced soil moisture. In spite of the retention of N in the ecosystem which might be interpreted as an indication of N limitation of vegetation growth, the export of N is only a little lower than in various Central American and Caribbean streams draining tropical montane forests where  $0.6\text{--}1.0 \text{ g m}^{-2} \text{ yr}^{-1}$  were observed which is at the upper end of N-loaded temperate streams [Brookshire *et al.*, 2012].

[22] Our results demonstrate that the water-bound N cycle of a remote tropical montane rain forest in Ecuador became increasingly inorganic in the last decade. We suggest that this inorganic turn of the N cycle can at least be partly attributed to increasing N deposition from the atmosphere, particularly in inorganic form. This would parallel a similar, earlier development in the industrialized parts of the temperate zone [Van Breemen, 2002]. Furthermore, climate change-related increased dryness likely affected N transformation processes, resulting in increasing fractional contributions of  $\text{NO}_3^-$  to TN concentrations in the ecosystem fluxes of the above-ground part of the ecosystem (including forest canopy and organic layer) and of  $\text{NH}_4^+$  in the belowground part. Reduced humidity might also have contributed to decreasing DON concentrations because of enhanced microbial DON consumption. All these changes occurred in only one decade.

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